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(54) PRODUCTION OF FLAMEPROOF POLYURETHANE FOAM RESINS

(71) We, BAYER AKTIENGESELLSCHAFT, formerly known as Farbenfabriken Bayer Aktiengesellschaft, a body corporate organised under the laws of Germany of 509 5 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of polyurethane foams, which are flameproof. This invention is a modification of or an improvement in the invention described in our patent application No. 1,267,011 15 (herein termed the Main Patent).

The Main Patent relates to a process for the production of a polyurethane foam which comprises reacting:

(a) at least one polyether which contains at least 2 reactive hydrogen atoms and has a molecular weight of 1,500 to 20, 10,000 and in which at least 10% of the hydroxyl groups present are primary hydroxyl groups,
 (b) at least one polyisocyanate solution which is a solution of at least one polyisocyanate which contains at least one isocyanuric acid ring dissolved in a monomeric polyisocyanate which is free from isocyanurate groups, and
 (c) a blowing agent.

In the course of further development on the process of the Main Patent it has now 35 been found that flame-proof polyurethane foams can also be produced with unexpectedly advantageous properties if, instead of using the polyisocyanates specified in the Main Patent, there are used 1 to 80% by weight 40 solutions (preferably 5 to 60% by weight

solutions) of polyisocyanates which contain at least one isocyanuric acid ring, (i.e. isocyanurate group) and, if desired, additional urethane groups in polyisocyanate which contain urethane groups and which are free from isocyanurate groups. If desired, monomeric isocyanates which contain neither isocyanurate groups nor urethane groups, may be added as solvents.

The reactants used for the production of the foam resins are otherwise the same as those used in the Main Patent. Accordingly the invention provides a process for the production of a polyurethane foam which comprises reacting:—

(a) at least one polyether which contains at least two reactive hydrogen atoms and has a molecular weight of 1,500 to 10,000 and in which at least 10% of the hydroxyl groups are primary hydroxyl groups.
 (b) at least one polyisocyanate solution which is a 1 to 80% solution by weight of at least one polyisocyanate which comprises at least one isocyanurate ring dissolved in at least one polyisocyanate which is free from isocyanurate groups but which comprises urethane groups.
 (c) a blowing agent.

The polyisocyanates which contain isocyanurate groups and also, if desired, urethane groups may be those polyisocyanates given in the Main Patent which contain at least one isocyanuric acid ring.

In many cases, however, it is desirable to react these polyisocyanates with less than equivalent quantities of compounds of molecular weight 31 to 10,000 which contain hydroxyl groups additional urethane groups thus being introduced into the polyisocyanate

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component. This enables the storage stability of the polyisocyanate used according to the invention to be improved.

The polyisocyanates used according to the invention which are employed in the form of the specified solutions, therefore contain at least one isocyanuric acid ring and, if desired, additional urethane groups. The introduction of the urethane groups may be effected before and/or after formation of the isocyanuric acid ring.

The compounds of molecular weight 31 to 10,000 which contain hydroxyl groups may be monofunctional, bifunctional, trifunctional, and higher functional hydroxyl compounds of conventional type. Methanol, butanol, oleyl alcohol and stearyl alcohol are given as examples of monofunctional hydroxyl compounds. It is preferred, however, to use bis-functional to octafunctional hydroxyl compounds, e.g. ethylene glycol, trimethylolpropane, pentaerythritol, sorbitol polyesters, and polyethers which contain hydroxyl groups, e.g. also polyethers which are obtained by the reaction of ethylene oxide and/or propylene oxide in the presence of polyfunctional initiator molecules such as water, alcohols or amines, including sucrose. The hydroxyl compounds preferably have a molecular weight of from 60 to 5000.

The solvents used for the polyisocyanate which contains at least one isocyanuric acid ring and, if desired, also urethane groups may be, as already mentioned above, the polyisocyanates already mentioned in the Main Patent which are free from isocyanurate groups and contain urethane groups and also, if desired, those monomeric polyisocyanates which are free from isocyanurate groups and from urethane groups.

The polyisocyanates which are free from isocyanurate groups and contain urethane groups may be prepared from conventional aliphatic, cycloaliphatic, araliphatic and aromatic polyisocyanates, e.g. hexamethylene diisocyanate, cyclohexane - 1,3 - and 1,4 - diisocyanate, tolylene - 2,4 - and/or - 2,6 - diisocyanate, 4,4' - diphenylmethanediisocyanate and m- and p-xylylene diisocyanate.

The following compounds are given as examples of polyhydroxyl compounds which may be used with the polyisocyanates for the preparation of the polyisocyanates which are free from isocyanurate groups and which contain urethane groups: butane - 1,3 - diol, butane - 1,4 - diol, diethyleneglycol, triethylene glycol, propane - 1,2 - diol, dipropylene glycol, tripropyleneglycol, 2,3-dimethylpentanediol, 2,2 - dimethylpropane - 1,3 - diol, pentane - 1,5 - diol, hexane - 2,5 - diol, 3 - methyl - pentane - 2,4 - diol, 2,2' - dihydroxydiethylsulphide, octadecane - 1,2 - diol, octaethyleneglycol, 4,4' - dihydroxy - dicyclohexyl - dimethylmethane, 1,5 - dihydroxy - decahydronaphthalene, 1,4 - dihydroxy - cyclohexane, hydroquinone, resorcinol, 4,4' - dihydroxydiphenyl - dimethylmethane, 4,4' - dihydroxydiphenyl - carbonate, 2,2' - dihydroxy - diphenyl, 4,4' - dihydroxy - octachlorodiphenyl - dimethylmethane, 1,5 - dihydroxy - naphthalene, glycerol, trimethylolpropane, hexanetriol, polyphenols according to U.S. Patent Specification No. 3,330,781, phloro-glucinol, pyrogallol, oxyhydroquinone; trihydroxytriphenylmethanes and their perhydrogenated analogues, pentaerythritol, sorbitol, mannitol, dulcitol, tetrosene, pentose, hexosene, disaccharides such as sucrose or cellulose, reaction products of polyhydric alcohols with at least one mol of an alkylene oxide such as ethylene oxide, propylene oxide, butylene oxide or styrene oxide, glycidol or mixtures of such epoxides to produce hydroxyl containing polyethers with hydroxyl numbers of 28 to 1500. The hydroxyl containing components for the reaction with polyisocyanates to produce urethane containing polyisocyanates may also be phenol formaldehyde condensation products, e.g. those prepared from phenol and formaldehyde in a molar ratio of 1:0.8, or polyesterpolyols with hydroxyl numbers of 35 to 650 prepared from linear and/or branched polyhydric alcohols. These compounds also include naturally occurring plant oils which contain free hydroxyl groups, e.g. castor oil.

Urethane containing polyols obtained from the above mentioned hydroxyl compounds and aliphatic, aromatic and/or araliphatic polyisocyanates may also be used as components for the preparation of the polyisocyanates which contain urethane groups.

Hydroxylalkylphosphorous acid esters or hydroxylalkylphosphoric acid esters may also advantageously be used.

The following are examples of suitable polyols which contain amide groups: Acid amides of diethanolamine or diisopropanolamine and aliphatic or aromatic dicarboxylic acids or hydroxycarboxylic acid such as glycolic acid, lactic acid, salicylic acid, p-hydroxybenzoic acid and hydroxylalkylbenzene carboxylic acids. The polyols which contain amide groups may also be prepared by reacting acid amides or low molecular weight polyamides with epoxides such as ethylene oxide, propylene oxide, butylene oxide, styrene oxide or mixtures thereof. Epoxide addition products with ammonia, substituted or unsubstituted hydrazines, primary aliphatic, cycloaliphatic, aromatic or araliphatic amines may also be used according to the invention.

Polyols suitable for use according to the invention may also be prepared by reacting diethanolamine, diisopropanolamine and other open chain or cyclic hydroxylalkylamines which have NH groups with ethylene glycol

carbonate to produce polyfunctional hydroxyalkylurethanes.

Mannich condensation products of CH acidic compounds, alkylphosphorus acid esters, 5 formaldehyde and secondary amines which contain hydroxyl groups may also be used.

The polyisocyanates which contain urethane groups are prepared by reacting the reactants at an NCO/OH ratio greater than 1 10 and then optionally dissolving the reaction product in monomeric diisocyanate to obtain the required concentration.

The prepolymer (polyisocyanate containing urethane groups) may subsequently be dissolved in the same polyisocyanate which was used for preparing it although it may also be advantageous to prepare the prepolymer with a less reactive polyisocyanate, e.g. an aliphatic, cycloaliphatic or araliphatic diisocyanate, and then to dissolve it in an aromatic diisocyanate. The reactive isocyanate groups present in such a polyisocyanate which contains urethane groups are highly differentiated in their reactivity, and the structure 20 of the high molecular weight polyurethane can be additionally influenced at the stage of foaming by suitable choice of these isocyanate groups if control of the foaming process by means of catalysts and/or additives alone 25 is not sufficient.

The polyisocyanate solutions which contain urethane groups may also be prepared in a single stage operation by reacting the polyols with excess polyisocyanates; the polymers can be adjusted to any desired concentration in this process.

The foam resin produced according to the invention have a higher bond strength on textiles and non-textile substrates when applied by flame backing.

The foam resin produced according to the invention also have an improved response to high frequency welding.

The foam resins produced by the process 45 according to the invention can be used, for example, as upholstery material, mattresses, packaging material, shock absorbing motor car parts, foils for backing or for high frequency welding and insulating materials. The 50 parts used may either be produced by foaming in the mould or they may be manufactured from material which has been foamed in the block.

In the course of our development work 55 on the process of the Main Patent, we have also found another modification or improvement in which component (b) is a 1 to

80% by weight solution of one or more polyisocyanates which contain at least one isocyanurate group and which have been reacted with a less than equivalent amount of at least one hydroxyl containing compound having a molecular weight of 31 to 10,000 the solution being in at least one monomeric polyisocyanate free from isocyanurate groups. This is described and claimed in our copending application No. 49600/71, (Serial No. 1337660).

The invention is illustrated by the following Examples.

Example 1

100 Parts by weight of polypropylene glycol (component (a)) which has been initiated on trimethylolpropane and tipped with ethylene oxide to produce approximately 72% of primary hydroxyl groups in end positions with an OH number of 38.1, 75
0.3 parts by weight of triethylene diamine, 2.5 parts by weight of water (blowing agent) and 80
53 parts by weight of a polyisocyanate solution (component b)) which consists of 95% of an isocyanate which contains urethane groups and 5% of a polymeric tolylene - 2,4 - diisocyanate which contains isocyanurate groups (NCO content 21.1%) are reacted together. The isocyanate which contains urethane groups was prepared as follows:

79 Parts by weight of a mixture of 70% by weight of trimethylolpropane and 30% by weight of butane - 1,3 - diol are reacted with 921 parts by weight of an isomeric tolylene diisocyanate mixture (65% of 2,4 - diisocyanatotoluene and 35% of 2,6 - diisocyanatotoluene) at 80 to 100°C and unreacted diisocyanate is then removed by distillation to yield a polyurethane which contains approximately 17% by weight of NCO groups. 40% by weight of this product, which is in the form of a solid resin, are dissolved in 60 parts by weight of an isomeric tolylene diisocyanate mixture (80% 2,4- and 20% 2,6-isomer); the clear solution obtained has an NCO content of 35.5% and a viscosity of 140 cP at 25°C. 95

The above mentioned components were mixed together. Foam formation begins after an induction period of 10 seconds and is completed after an expanding time of 75 seconds. The highly elastic foam resin obtained has the following properties:

	Density according to DIN 53420	40 kg/m ³	
	Tensile strength according to DIN 53571	0.9 kg wt/cm ²	
5	Elongation at break according to DIN 53571	180%	
	Compression strength at 40% compression according to DIN 53577	27 p/cm ²	
	Flammability test according to ASTM D 1692/67 T	3.0	
10	Average length of burnt sample (cm)	16	
	Average extinction time (sec)		
	The foam resin is therefore to be regarded as self-extinguishing.		
	Example 2		
15	100 Parts by weight of a polypropylene glycol which has been initiated on trimethylolpropane and tipped with ethylene oxide to produce approximately 72% of primary hydroxyl groups in end positions with an OH number of 38.1, 0.3 parts by weight of triethylene diamine, 2.5 parts by weight of water and 48 parts by weight of an isocyanate mixture which consists of 95% of an isocyanate which contains urethane groups (see A—below) and 5% of a 2,4- and 2,6-tolylene diisocyanate containing urethane groups and isocyanurate groups (see B—below) (NCO content 38.9%) are reacted together. The isocyanate which contains urethane groups was prepared as follows:		
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35	A.—A polyurethane which contains approximately 17% by weight of NCO groups is prepared by reacting 79 parts by weight of a mixture of 70% by weight of trimethylol propane and 30% by weight of butane - 1,3 - diol with 921 parts by weight of an isomeric tolylene diisocyanate mixture (65% of 2,4 - diisocyanatotoluene and 35% of 2,6 - diisocyanatotoluene) at 80 to 100°C. and then removing the unreacted diisocyanate by distillation. 40 Parts by weight of this product which is in the form of a solid resin are dissolved in 60 parts by weight of an isomeric tolylene diisocyanate mixture (80% 2,4- and 20% 2,6-		
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85	Density DIN 53420	(kg/m ³)	40
	Tensile strength according to DIN 53571	(kg wt/cm ²)	0.8
	Elongation at break according to DIN 53571	(%)	130
	Compression test DIN 53577	(p/cm ²)	30
	Inflammability according to ASTM D 1692—67T		
90	Average length of burnt sample (cm)		3.5
	Average extinction time (sec)		18
	Assessment		self-extinguishing
	isomer). The clear solution obtained has an NCO content of 35.5% and a viscosity of 140 cP at 25°C. The polyisocyanate which contains isocyanurate groups was prepared as follows:		50
	B.—1.96 Parts by weight of 1,2-propylene glycol are added to 35 parts by weight of an 80:20 percent by weight isomeric mixture of 2,4- and 2,6-tolylene diisocyanate at 60°C and the compounds are left to react together for 30 minutes during which time the reaction mixture heats up to 80°C. After the addition of 0.037 parts by weight of β -phenylethyl-ethyleneimine, the reaction mixture is heated to 130°C and it is left at this temperature, at which it undergoes trimerisation to form isocyanurate groups, until an NCO value of 30% is reached, which requires about 1 to 2 hours. After cooling to 100°C. 3.7 parts by weight of tripropylene glycol are added and the reaction is left to proceed for one hour at the same temperature. The reaction mixture, which has an NCO value of 23.3% at the end of this time, is then diluted with 65.06 parts by weight of an 80/20 mixture of 2,4- and 2,6-tolylene diisocyanate. The polyisocyanate solution obtained has the following properties:		55
	% NCO=38.9, cP _{25deg.} =39, n _D ²⁰ =1.5642		60
			65
	A foam resin which has the following mechanical properties is obtained:		70
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			80

Example 3

5 100 Parts by weight of a polypropylene glycol which has been initiated on trimethylolpropane and tipped with ethylene oxide to produce approximately 72% of primary hydroxyl groups in end positions with an OH number of 38.1, 0.3 parts by weight of triethylenediamine, 2.5 parts by weight of water, and

10 48 parts by weight of an isocyanate mixture which consists of 95% of isocyanate which contains urethane groups and 5% of a 2,4- and 2,6-tolylene diisocyanate mixture which contains urethane groups and isocyanurate groups (NCO content 39.0%) are reacted together.

The urethane isocyanate was prepared as given in Example 2-A.

The polyisocyanate which contains isocyanurate groups was prepared using the same method as in Example 2B but adding 2.03 parts of trimethylol propane instead of tripropylene glycol and diluting the reaction mixture with 66.30 parts of an 80/20 mixture of 2,4- and 2,6-tolylene diisocyanate. This yielded a polyisocyanate solution which has the following properties:

$$\% \text{ NCO} = 39.0, cP_{25\text{deg.}} = 58, n_D^{50} = 1.5682.$$

A foam resin which has the following mechanical properties is obtained:

35	Density DIN 53420	(kg/m ³)	40
	Tensile strength according to DIN 53571	(kg/wt/cm ²)	1.0
	Elongation at break according to DIN 53571	(%)	150
	Compression test DIN 53577	(p/cm ²)	30
40	Inflammability according to ASTM D 1692-67 T		
	Average length of burnt sample (cm)		3.8
	Average extinction time (sec)		22
	Assessment		self-extinguishing

Example 4

45 100 Parts by weight of a polypropylene glycol which has been initiated on trimethylolpropane and tipped with ethylene oxide to produce approximately 72% of primary hydroxyl groups in end position with an OH number of 38.1, 0.3 Parts by weight of triethylenediamine, 2.5 parts by weight of water, and

50 46 parts by weight of an isocyanate mixture which consists of 95% of an isocyanate which contains urethane groups and 5% of a 2,4-tolylene diisocyanate (NCO content 39.4%) which contains urethane groups and isocyanurate groups are reacted together.

The isocyanate which contains urethane groups was prepared as in Example 2-A.

60 The polyisocyanate which contains isocyanurate groups was prepared as follows:

B.—1.54 Parts of 1,2-propylene glycol are added to 38.46 parts of tolylene - 2,4 - diisocyanate at 60°C in a vessel equipped with a stirrer under nitrogen (used as

protective gas), and the reactants are left to react together for 30 minutes, during which time the mixture heats up to 95 to 100°C without external supply of heat. After the addition of 0.060 of β - phenylethyl - ethyleneimine, the reaction mixture is heated to 130°C and left at this temperature until, after about 5 to 6 hours, the NCO content is 26.0%. Trimerisation of the polyisocyanate is then stopped by the addition of 0.038 parts of methyl p-toluenesulphonate, and the reaction mixture is diluted with 60.00 parts of an 80/20 mixture of 2,4- and 2,6-tolylene diisocyanate after it has been cooled to 120°C. The reaction mixture is characterised by the following properties:

$$\% \text{ NCO} = 39.4, cP_{25\text{deg.}} = 63, n_D^{50} = 1.5721.$$

65	Density DIN 53420	(kg/m ³)	41
90	Tensile strength according to DIN 53571	(kg wt/cm ²)	1.0
	Elongation at break according to DIN 53571	(%)	160
	Compression test DIN 53577	(p/cm ²)	28
95	Inflammability according to ASTM D 1692-67 T		
	Average length of burnt sample	(cm)	3.3
	Average extinction time	(sec)	27
	Assessment		self-extinguishing

Example 5

5 100 Parts by weight of a polypropylene glycol which has been initiated on trimethylol propane and tipped with ethylene oxide to produce approximately 72% of primary hydroxyl groups in end position with an OH number of 38.1,

10 0.3 parts by weight of triethylenediamine, 2.5 parts by weight of water and 48 parts by weight of an isocyanate mixture consisting of 95% of an isocyanate which contains urethane groups and 5% of a mixture of urethane-containing and isocyanurate-containing 2,4- and 2,6-toluylene diisocyanate and 4,4'-diphenylmethane diisocyanate (NCO content 38.40%) are reacted together.

20 The isocyanate which contains urethane groups was prepared as given in Example 2-A.

The polyisocyanate which contains iso-

45 Density DIN 53420
Tensile strength according to DIN 53571
Elongation at break according to DIN 53571
Compression test DIN 53577
Inflammability according to ASTM D 1692—67 T

50 Average length of burnt sample
Average extinction time
Assessment

55 Example 6
The following components are introduced into the mixing chamber of a foaming machine:

60 100 Parts by weight of a polypropylene glycol which has been initiated on trimethylolpropane and tipped with ethylene oxide to produce approximately 72% of primary hydroxyl groups in end positions with an OH number of 38.1,

65 0.2 parts by weight of triethylenediamine, 0.2 parts by weight of N,N',N'' - pentamethyl - diethylene triamine, 2.5 parts by weight of water, 2.0 parts by weight of butane - 1,4 - diol and

90 Density according to DIN 53520
Tensile strength according to DIN 53571
Elongation at break according to DIN 53571
Compression strength at 40% compression according to DIN 53577
Inflammability test according to ASTM D 1692/67 T

95 Average length of burnt sample (cm) 3.5
Average extinction time (sec) 25

cyanurate groups was prepared as follows:

25 20 parts of 1,2-propylene glycol are added to a mixture of 225 parts of an 80/20 mixture of 2,4- and 2,6-toluylene diisocyanate and 275 parts of 4,4'-diphenylmethanediisocyanate at 60°C and the reactants are reacted together for 30 minutes. After the addition of 1 part of β -phenylethylethyleneimine, the reaction mixture is heated to 130°C. The trimerisation which takes place at this temperature is stopped after 2½ hours, when the NCO content of the reaction mixture is 26.5%, by the addition of 1 part of methyl p-toluenesulphonate. After dilution with 624 parts of an 80/82 mixture of 2,4- and 2,6-toluylene diisocyanate a polyisocyanate which has the following properties is obtained:

$$\% \text{ NCO} = 38.4, cP_{25\text{deg.}} = 24, nD^{20} = 1.5738. \quad 40$$

A foam resin which has the following mechanical properties is obtained:

Density DIN 53420	(kg/m ³)	38
Tensile strength according to DIN 53571	(kg/wt/cm ²)	1.1
Elongation at break according to DIN 53571	(%)	160
Compression test DIN 53577	(p/cm ²)	30
Inflammability according to ASTM D 1692—67 T		
Average length of burnt sample	(cm)	40
Average extinction time	(sec)	27
Assessment		self-extinguishing

70 34.5 parts by weight of an isocyanate mixture consisting of 93% by weight of toluylene diisocyanate (80% of 2,4- and 20% of 2,4-isomer), 2% by weight of 2,4-toluylene diisocyanate which contains isocyanurate groups (NCO content 21.1%) and 5% by weight of an isocyanate which contains urethane groups (NCO content 35.8%, viscosity 77.8 cP at 25°C) and which has been obtained by reacting propoxylated trimethylolpropane (OH number 875) with toluylene diisocyanate (80% 2,4- and 20% 2,6-isomer) at 80 to 100°C. 75 80

85 A highly elastic foam resin which has the following properties is obtained: 85

Density according to DIN 53520	39 kg/m ³
Tensile strength according to DIN 53571	1.0 kg wt/cm ²
Elongation at break according to DIN 53571	190%
Compression strength at 40% compression according to DIN 53577	26 p/cm ²

The foam resin is therefore to be regarded as self-extinguishing.

Example 7

100 Parts by weight of a polypropylene glycol which has been initiated on trimethylolpropane tipped with ethylene oxide to produce approximately 72% of primary hydroxyl groups in end positions with an OH number of 38.1; 0.3 parts by weight of triethylenediamine, 2.5 parts by weight of water, 10 4.0 parts by weight of butane - 1,4 - diol and 4.0 parts by weight of tris-(dipropylene-glycol)phosphite are mixed together and 15 69.5 parts by weight of an isocyanate mixture consisting of 55% by weight of tolylene diisocyanate (80% 2,4- and 20% 2,6-isomer), 5% by weight of polymeric

2,4-tolylene diisocyanate which contains isocyanurate groups (NCO content 21.1%) and 40% of an isocyanate which contains urethane groups (NCO content 32.9%, viscosity 808 cP at 25°C) and which was obtained by reacting propoxylated glycerol (OH number 1100) with tolylene diisocyanate (80% 2,4- and 20% 2,6-isomer) at 80 to 100°C. 20 25

are added to the mixture.

Foam formation begins after an induction period of 10 seconds and is completed after 90 seconds. A soft, highly elastic foam resin is obtained which has the following properties:

35	Density according to DIN 53420	41 kg/m ³
	Tensile strength according to DIN 53571	0.8 kg wt/cm ²
	Elongation at break according to DIN 53571	170%
40	Compression strength at 40% compression according to DIN 53577	23 p/cm ²
	Inflammability test according to ASTM D 1692/67 T	
	Average length of burnt sample (cm)	3.1
	Average extinction time (sec)	43

The foam resin is therefore to be regarded as self-extinguishing.

Example 8

45 100.0 Parts by weight of a polypropylene-glycol which has been initiated on propylene glycol and tipped with ethylene oxide to produce approximately 67% of primary hydroxyl groups in end positions with an OH number of 28.0, 50 3.0 parts by weight of water, 0.2 parts by weight of dimethylamino-ethanol and 55 1.0 part by weight of triethylamine are mixed together and reacted with

57.7 parts by weight of an isocyanate mixture has an NCO content of 28.9% and consists of 18 parts by weight of an isocyanate-containing adduct (NCO content (31.7%) of tripropylene glycol and 2,4- and 2,6-tolylene diisocyanate of which 80.0% is 2,4-tolylene diisocyanate, and 20 parts by weight of a polymeric 2,4-tolylene diisocyanate which contains isocyanate groups (NCO content 21.1%): 60 65

A foam resin which has the following mechanical properties and flame resistance is obtained:

70	Density according to DIN 53420	37 kg/m ³
	Tensile strength according to DIN 53571	1.2 kg wt/cm ²
	Elongation at break according to DIN 53571	195%
75	Compression strength at 40% compression according to DIN 53577	34 p/cm ²
	Inflammability according to test ASTM D 1692/67 T	
	Average length of burnt sample (cm)	2.5
	Average extinction time (sec)	23
80	Assessment of the foam resin	self-extinguishing

Example 9

100.0 Parts by weight of a polypropylene glycol which has been initiated on propylene glycol and tipped with ethylene oxide to produce approximately 67% of primary hydroxyl groups in end positions with an OH number of 28.0, 85 3.0 parts by weight of water, 0.2 parts by weight of dimethylamino-ethanol and

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1.0 part by weight of triethylamine are mixed together and reacted with 50.4 parts by weight of an isocyanate mixture which has an NCO content of 33.1% and which consists of 80.0 parts by weight of an isocyanate-containing adduct (NCO content 31.7%) of tripropylene glycol and 2,4- and 2,6-tolylene diisocyanate comprising 80% of 2,4-tolylene diisocyanate and of 20.0 parts by weight of a urethane-containing and isocyanurate-containing 2,4- and 2,6-tolylene diisocyanate (80:20, NCO content 38.50%) which was prepared as follows:

1.33 Parts of 1,2 - propylene glycol are added to 27.50 parts of an 80/20 mixture of 2,4- and 2,6-tolylene diisocyanate at 60°C, and after a reaction time of 30 minutes, dur-

ing which the reaction mixture heats up to 80°C, 0.044 part of β -phenylethylethyleneimine is added. Using nitrogen as protective gas, the reaction mixture is then heated to 130°C. and trimerisation is stopped after a reaction time of about 5 hours at this temperature by adding 0.042 parts of benzoyl chloride, the NCO value being then 25.8%. After dilution of the reaction mixture with 71.50 parts of a 65/35 mixture of 2,4- and 2,6-tolylene diisocyanate, 5.28 parts of 2,3-dibromopropanol are added to this solution and the solution is then reacted for 2 hours at 80 to 90°C. The modified polyisocyanate solution has the following properties:

% NCO=38.5, $cP_{25deg.}=26$, $n_D^{20}=1.5690$. 35

A foam resin which has the following mechanical properties is obtained:

40	Density DIN 53420 Tensile strength according to DIN 53571 Elongation at break according to DIN 53571 Compression test DIN 53577	(kg/m ³)	36
45	Inflammability according to ASTM D 1692-67 T Average length of burnt sample Average extinction time Assessment	(kg wt/cm ²) (%) (p/cm ²) (cm) (sec)	1.3 200 35 4.0 25 self-extinguishing

Example 10

50 100.0 Parts by weight of a polypropylene glycol which has been initiated on propylene glycol and tipped with ethylene oxide to produce approximately 67% of primary hydroxyl groups in end positions with an OH number of 28.0, 55 3.0 parts by weight of water, 0.2 parts by weight of dimethylaminoethanol and 60 1.0 part by weight of triethylamine are mixed together and reacted with 50.4 parts by weight of an isocyanate mixture which has an NCO content of 33.10% and which consists of 80.0 parts by weight of an isocyanate-containing adduct (NCO content 31.7%) of tripropylene glycol and 2,4- and 2,6-tolylene diisocyanate comprising 80% of 2,4-tolylene diisocyanate, and 20.0 parts by weight of a mixture of 2,4- and 2,6-tolylene diisocyanate which contains urethane groups and isocyanurate groups (80:20, NCO content 32.20%). The tolylene diisocyanate mixture which contains urethane groups and isocyanurate groups was prepared as follows:

75 0.40 Parts of a solution of water in acetone

(25 g of water made up to 1000 ml with acetone) and 0.038 parts of β - phenylethylethyleneimine are added to 25.00 parts of an 80/20 mixture of 2,4 and 2,6-tolylene-diisocyanate at 22°C. The slightly exothermic trimerisation reaction of diisocyanate starts after a brief induction period and it is stopped after a reaction time of about 2 to 2½ hours, when the NCO content is 31.0% and the reaction temperature 70°C, by the addition of 0.204 parts by weight of methyl p-toluenesulphonate. With the reaction mixture at a temperature of 80°C, 3.00 parts by weight of tripropylene glycol are added and the reaction is left to proceed for 1½ hours at the same temperature. After the addition of 75 parts by weight of a mixture which consists of 2,4- and 2,6-tolylene diisocyanate in the ratio of 80:20% by weight and intensive homogenisation of the reactants, 5.42 parts by weight of 2,3-dibromopropanol are added at 90°C. After a reaction time of 2 hours at 90 to 100°C, the polyisocyanate combination has the following properties:

% NCO=38.2, $cP_{25deg.}=33.0$, $n_D^{20}=1.5790$.

A foam resin which has the following mechanical properties is obtained:

5	Density DIN 53420 Tensile strength according to DIN 53571 Elongation at break according to DIN 53571 Compression test DIN 53577 Inflammability according to ASTM D 1692-67 T	(kg/m ³) 36 (kg wt/cm ²) 1.1 (%) 170 (p/cm ²) 40
10	Average length of burnt sample Average extinction time Assessment	(cm) 3.8 (sec) 31 self-extinguishing
15	Example 11 100.0 Parts by weight of a polypropylene glycol which has been initiated on propylene glycol and tipped with ethylene oxide to produce approximately 67% of primary hydroxyl groups in end positions with an OH number of 28.0,	has an NCO content of 26.2% and which consists of 79.5% by weight of an isocyanate containing adduct (NCO content 27.62%) of tripropylene glycol and 2,4- and 2,6-tolylene diisocyanate comprising 80% of 2,4-tolylene diisocyanate and 4,4'-diisocyanatediphenylmethane in the ratio of 3:2 and 20.5 parts by weight of a polymeric 2,4-tolylene diisocyanate which contains isocyanurate groups (NCO content 21.1%).
20	3.0 parts by weight of water, 0.2 parts by weight of dimethylaminomethanol and 1.0 part by weight of triethylamine	
25	and mixed together and reacted with 63.5 parts by weight of an isocyanate which	A foam resin which has the following mechanical properties and flame resistance is obtained:
40	Density according to DIN 53420 Tensile strength according to DIN 53571 Elongation at break according to DIN 53571	40.0 kg/m ³ 1.1 kg wt/cm ²
45	Compression strength at 40% compression according to DIN 53577 Inflammability according to ASTM D 1692/67 T Average extinction time	160% 43 p/cm ² 22 sec.
50	Example 12 100.0 Parts by weight of a polypropylene glycol which has been initiated on propylene glycol and tipped with ethylene oxide to produce approximately 67% of primary hydroxyl groups in end positions with an OH number of 28,	in the ratio of 3:2 and 20.5 parts by weight of a 2,4-tolylene diisocyanate (NCO content 39.5%) which contains urethane groups and isocyanurate groups.
55	3.0 parts by weight of water, 0.2 parts by weight of dimethylaminomethanol and 1.0 part by weight of triethylamine	The polyisocyanate which contains urethane groups and isocyanate groups was prepared as follows:
60	are mixed together and reacted with 55.5 parts by weight of a polyisocyanate solution which has an NCO content of 30.2% and which consists of 79.5 parts by weight of an isocyanate-containing adduct (NCO content 27.62% of tripropylene glycol and a mixture of 2,4- and 2,6-tolylene diisocyanate containing 80% of 2,4-tolylene diisocyanate and 4,4'-diisocyanatodiphenyl methane	0.061 Parts by weight of a solution of water in acetone (25 g of water made up to 1000 ml with acetone) and 0.058 parts by weight of β -phenylethyl-ethylenimine are added to 38.76 parts by weight of tolylene-2,4-diisocyanate at 25°C. The slightly exothermic trimerisation reaction of diisocyanate starts after a brief induction period. It is stopped after about 2 hours, at an NCO content of 31.0 to 31.3%, by the addition of 0.042 parts by weight of benzoyl chloride. The reaction mixture is then heated to 80°C and 2.33 parts by weight of tripropylene glycol are added in the course of 10 to
65		
70		

5 minutes, the reaction mixture reaching a temperature of 95 to 100°C. Stirring is then continued for one hour without any further supply of heat and the reaction mixture is then diluted with 58.91 parts by weight of an 80/20 mixture of 2,4- and 2,6-tolylene diisocyanate. The solution of the modified

isocyanurate polyisocyanate in tolylene diisocyanate has the following properties:

% NCO=39.5, cP_{25deg.}=54, n_D²⁰=1.5827. 10

A foam resin which has the following mechanical properties is obtained:

15	Density DIN 53420	(kg/m ³)	40
	Tensile strength according to DIN 53571	(kg wt/cm ²)	1.1
	Elongation at break according to DIN 53571	(%)	160
	Compression test DIN 53577	(p/cm ²)	40
20	Inflammability according to ASTM D 1692—67 T	(cm)	2.3
	Average length of burnt sample	(sec)	22
	Average extinction time		self-extinguishing
	Assessment		

Example 13

25 100.0 Parts by weight of a polypropylene glycol which has been initiated on propylene glycol and tipped with ethylene oxide to produce approximately 67% of primary hydroxyl groups in end positions with an OH number of 28, 3.0 parts by weight of water 0.2 parts by weight of dimethylamino-ethanol and 1.0 part by weight of triethylamine

35 are mixed together and reacted with

40 56.50 parts by weight of a polyisocyanate solution which has an NCO content of 29.4% and which consists of 79.5 parts by weight of an isocyanate-containing adduct (NCO content 27.62%) of tripropylene glycol and a mixture of 2,4- and 2,6-tolylene diisocyanate containing

60	Density DIN 53420	(kg/m ³)	39
	Tensile strength according to DIN 53571	(kg wt/cm ²)	0.9
	Elongation at break according to DIN 53571	(%)	160
65	Compression test DIN 53577	(p/cm ²)	30
	Inflammability according to ASTM D 1692—67 T	(cm)	2.8
	Average length of burnt sample	(sec)	15
70	Average extinction time		self-extinguishing
	Assessment		

WHAT WE CLAIM IS:—

1. A process for the production of a polyurethane foam which comprises reacting:—

75 (a) at least one polyether which contains at least two reactive hydrogen atoms and has a molecular weight of 1,500 to 10,000 and in which at least 10% of the hydroxyl groups are primary hydroxyl groups,

45 80% of 2,4-tolylene diisocyanate and 4,4'-diisocyanatodiphenylmethane in the ratio of 3:2 and 20.5 parts by weight of a polymeric 2,4-tolylene diisocyanate which contains isocyanurate groups (NCO content 36.0%) which was prepared as follows:

50 5 Parts by weight of 2,3-dibromopropanol are added to 95 parts by weight of the modified isocyanurate polyisocyanate described in Example 12 in tolylene diisocyanate at 90°C and the components are reacted at this temperature for 2 hours. The resulting polyisocyanate solution has the following properties:

% NCO=36.0, cP_{25deg.}=81, n_D²⁰=1.5858.

55 A foam resin which has the following mechanical properties is obtained:

(b) at least one polyisocyanate solution which is a 1 to 80% solution by weight of at least one polyisocyanate which comprises at least one isocyanurate ring dissolved in at least one polyisocyanate which is free from isocyanurate groups but which comprises urethane groups, (c) a blowing agent.

80 85 2. A process as claimed in Claim 1 in

which component (b) is a 5 to 60% by weight solution.

3. A process as claimed in Claim 1 or Claim 2 in which the said polyisocyanate 5 which comprises isocyanurate groups also comprises urethane groups.

4. A process as claimed in any of Claims 1 to 3 in which component (b) also comprises one or more monomeric isocyanates 10 which are free from both isocyanurate and urethane groups.

5. A process as claimed in Claim 1 sub-

stantially as herein described with reference to any one of the Examples.

6. Foam resins when produced by a process as claimed in any of Claims 1 to 5. 15

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